

Supporting Information

Kinetics of Fe(II)-Catalyzed Transformation of 6-line Ferrihydrite under Anaerobic Flow Conditions

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Coating of ferrihydrite onto glass microspheres

To coat ferrihydrite onto glass microspheres, 10ml of the synthesized 6-line ferrihydrite solution was added to 0.1g of the glass microspheres with solution ionic strength adjusted by adding appropriate amounts of reagent grade NaCl (EMD chemicals, Inc). After shaking overnight, the mixed solution was washed with D. I. water thoroughly through centrifugation and was further filtered through a 45 μm nylon filter to remove any unconsolidated, loosely coated particles. The ferrihydrite-coated micro-glass spheres obtained were stored in D. I. water in a polyethylene bottle prior to their use in the experiment. The Fe content in the packed capillary tube experiment system was about 0.008mg (quantified by completely dissolving the ferrihydrite coatings in sodium dithionite solution followed by ICP-MS analysis).

Capillary tube experimental setup

To set up the capillary tube experiments, the fused silica capillary tubing was first cut into 5 cm length individual tubes and plugged with Ti metal wire (100 μm O.D, McMaster Carr) at one end to hold the packed ferrihydrite-coated microspheres in place and to act as a filter (leaving about 5 μm void space) for the effluent solution. PFA Teflon tubing (150 μm I.D and 360 μm O. D., Upchurch Scientific) was used to deliver the input and effluent solutions. The ferrihydrite-coated microspheres were then packed into the capillary tubes under vacuum over a length of about 1 cm with D. I. water and connected to the input and output Teflon tubing through NanoPort fitting assemblies (Upchurch Scientific). The packed capillary tubes were then mounted on an aluminum sample holder for easy handling of the whole sample unit during the experiment. The assembled capillary tubes with the ferrihydrite-coated spheres were leak tested first and transferred inside the laboratory anaerobic chamber and thoroughly flushed with deoxygenated D. I. water for several days before starting injection of the experimental stock solutions. The flow rates were set at 0.5uL/min for all experiment conditions. Given that the pore volume of the capillary tubes, after correction for the volume of the spheres, was about 0.09 microliters, this corresponds to a residence time of about 10 seconds. At the end of the experiment, each reacted sample was thoroughly flushed with deoxygenated water for several hours before being disassembled inside the lab anaerobic chamber. The disassembled capillary samples were then sealed with epoxy at both ends and were stored inside small anaerobic boxes equipped with anaerobic sachets (Mitsubishi[®]) for transport to synchrotron beamlines for the sample analysis. Samples of higher concentration of Fe(II) injection (18mM and 1.8mM) were analyzed at ALS, while samples at 0.36mM Fe(II) injection were analyzed at SSRL. A schematic illustration of the experimental setup is given in Figure S1.

Effluent solution chemistry analysis

The effluent solution was analyzed for total Fe by ICP-MS equipped with a Dynamic Reaction Cell (DRCII, Perkin Elmer) using ammonium gas (ultrapure grade, 99.999%) to remove any

interferences, and also by a ferrozine method using UV-vis spectrophotometer for Fe(II). The limit of detection for Fe is around 1 ppb by ICP-MS and around 20 ppb by the ferrozine method. The Fe(III) in the effluent solution was determined by the difference between Fe(II) measured by ferrozine method and total Fe measured by ICP-MS. It was also determined by comparing the total Fe result in the effluent and the injection stock solution from ICP-MS analysis, which has a better detection limit. A speciation analysis based on the method developed by To et al. (1) was also attempted for effluent solution analysis. In this approach, ferrozine and acetohydroxamic acid reagents were used chelators for ferrous and ferric ions followed by separations with a C₁₈ cartridge and ICP-MS analysis. During the course of the experiment, effluent samples were collected periodically and passed through a 0.1 micron filter for solution analysis.

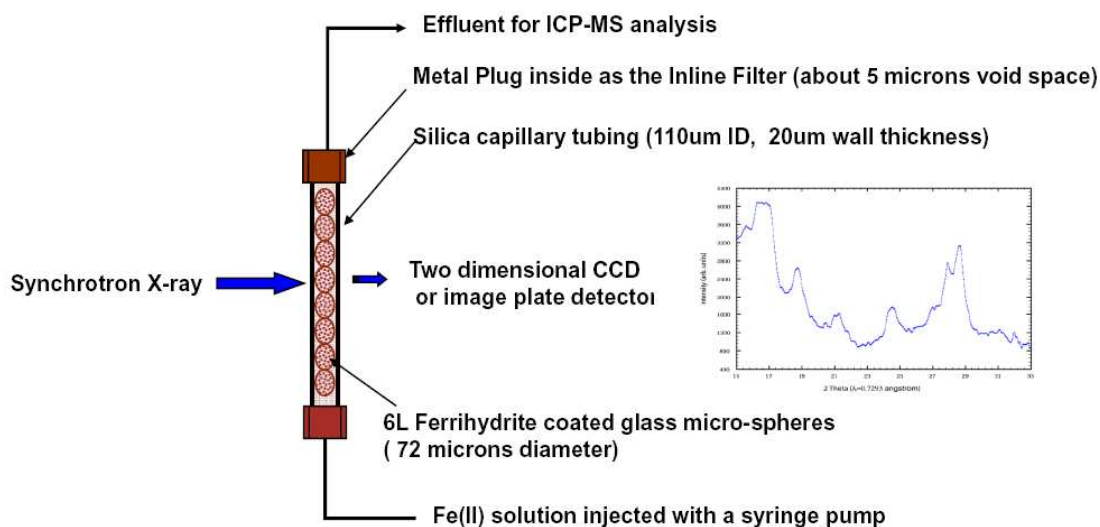
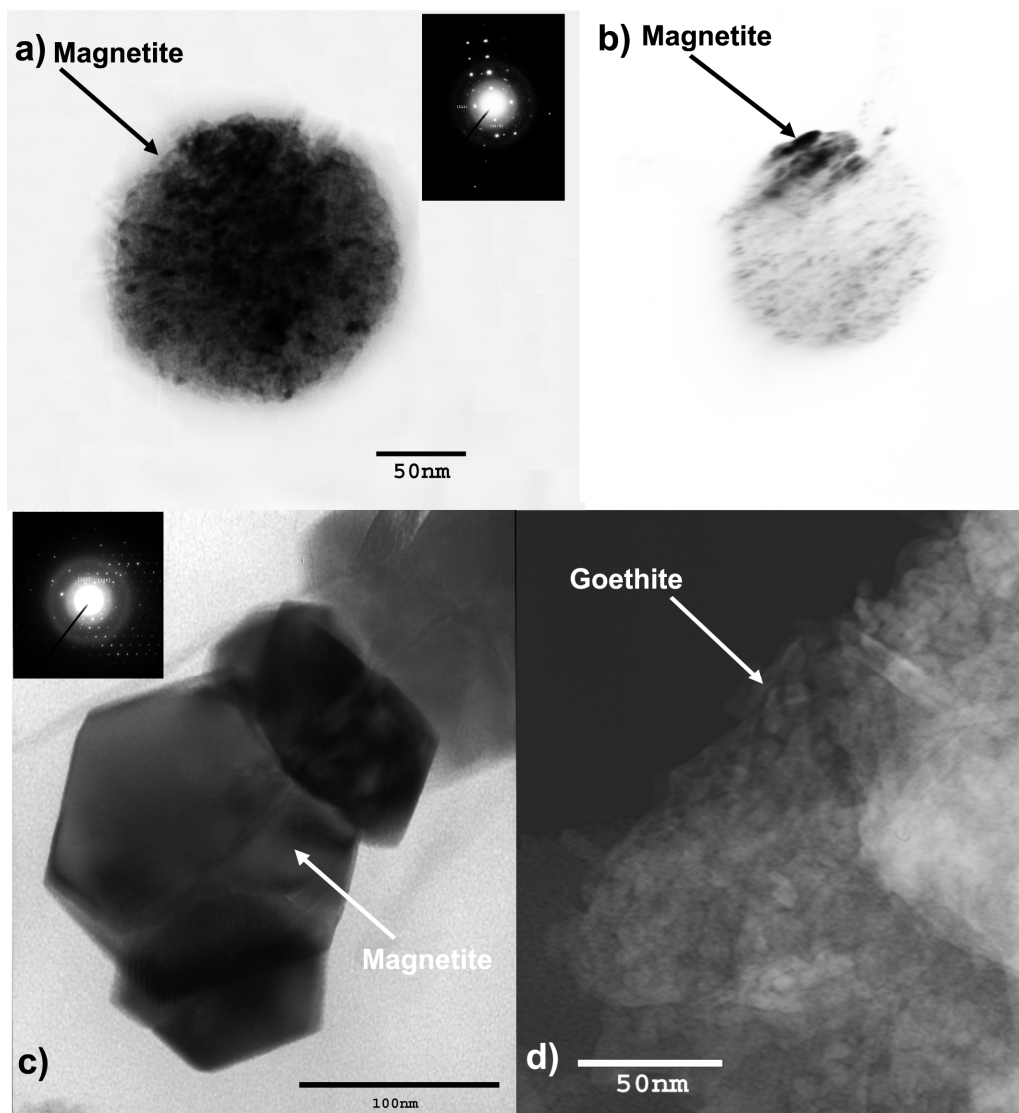


Figure S1. Schematic illustration of the experimental setup and the XRD pattern obtained for the initial 6-line ferrihydrite (on the right)



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88 Figure S2. TEM micrographs and SAED patterns of transformation products. (a) magnetite
 89 formed on samples reacted with 18 mM Fe(II) for 11 hours; (b) images of magnetite crystals on
 90 (a) showing [220] crystal face; (c) magnetite crystals formed after 28 hours of reaction with 18
 91 mM Fe(II); (d) goethite formed after reacting with 0.36 mM Fe(II) for 35 days.

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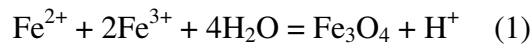
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Table S1. Gibbs energy of magnetite and goethite formation at the experimental conditions*

Input Fe(II) concentration	Magnetite (kJ/mol)	Goethite (kJ/mol)
18 mM	39.3	8.96
1.8 mM	35.3	8.96
0.36 mM	31.9	8.96

*The Gibbs energy of magnetite and goethite formation was calculated using the geochemical software PHREEQC according to following reactions:



The equilibrium constants for reaction (1) is calculated according to Gibbs energy of formation of magnetite (-1012.6 kJ/mol) and Gibbs energy of ferrous (-90.53 kJ/mol) and ferric (-16.28 kJ/mol) ions based on the data from Hemingway and Parker, et al. (2, 3). The equilibrium constant for reaction (2) is from the data of Cornell and Schwertmann (4). The concentrations of ferric ions in the experiment system are assumed to be supplied from the equilibrium solubility of 6-line ferrihydrite according to the data of Majzlan et al. (5).

Table S2. Summary of the Fe(II) adsorption on ferrihydrite at experimental conditions studied calculated with PHREEQC and using equilibrium constants from Appelo et al. (6)*.

Input Fe(II) (mM)	Hfo_wOFe+ (mole)	Hfo_sOFe+ (mole)	Hfo_wOFeOH (mole)	Total adsorbed Fe²⁺ (mole)
0.36	2.40E-09	6.45E-10	4.09E-10	3.45E-09
1.8	7.54E-09	6.88E-10	1.08E-09	9.31E-09
18	1.45E-08	6.98E-10	1.87E-09	1.70E-08

* Hfo_sOFe+, Fe(II) adsorption on strong sites of ferrihydrite; Hfo_wOFe+ and Hfo_wOFeOH, Fe(II) on weak sites of ferrihydrite. The total surface sites of the ferrihydrite packed in the capillary tube system are approximately 2.8×10^{-8} moles.

114 **Literature Cited**

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